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## $\text{Eu}^{3+}$ and $\text{Gd}^{3+}$ spectroscopy in fluoroindate glasses

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### Abstract

Luminescence data for  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  in fluoroindate glasses are compared to those of a fluorozirconate glass. Emission is observed from  $\text{Eu}^{3+}$   $^5\text{D}_J$  ( $J=0, 1, 2$  and  $3$ ) and  $\text{Gd}^{3+}$   $^6\text{P}_{7/2}$  excited-state levels and the results put in evidence Eu–Eu and Gd–Eu energy transfer processes. Vibronic bands related to a  $320\text{ cm}^{-1}$  vibrational mode could be observed for  $\text{Eu}^{3+}$  luminescent transitions with  $\Delta J=0, 1$  and  $2$  and also for the  $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$  transition of  $\text{Gd}^{3+}$ . Lanthanide ion site symmetry is closer to an inversion center in fluoroindate glasses than it is in fluorozirconate.

### 1. Introduction

There is a great interest in the study of rare-earths-doped heavy-metal fluoride glasses. The addition of these ions is known to increase the stability against devitrification and corrosion and the class of materials obtained has an increasing potential use in the laser and optical fiber communication industries [1].

Besides the well-known fluorozirconate glasses several systems based on indium fluoride have been studied [2]. One of the major interests of fluoroindate glasses lies in their low multiphonon absorption which enlarges the infrared spectroscopic range of utilization of fluoride glass up to  $7\text{--}8\text{ }\mu\text{m}$ . Therefore rare-earths-doped fluoroindate fibers are likely to be used to make new laser sources beyond  $3\text{ }\mu\text{m}$  and more efficient emitters between  $1$  and  $3\text{ }\mu\text{m}$ . Also as the multiphonon emission rate is lower in fluoroindates than in fluorozirconates glasses, the non-radiative energy transfers between close levels is reduced and some fluorescence transitions which are not observed in ZBLAN-doped glasses can be made active in these new compositions. It is thus important to in-

vestigate and understand the rare-earth spectroscopic properties in those media.

In this context it is interesting to use  $\text{Eu}^{3+}$  because of the simplicity of its electronic energy scheme and the sensitivity of the electronic transitions to changes in the local environment [3]. Some papers have been reported dealing with  $\text{Eu}^{3+}$  spectroscopy in fluorozirconate and fluoroberylate glasses [4–10]. Fluorescence line narrowing has been studied recently for barium–indium–gallium fluoride glass [11].

The vitreous region in the pseudo-ternary system  $\text{InF}_3\text{--ZnF}_2\text{--}(\text{SrF}_2\text{--BaF}_2)$  has been established by one of us [12]. It was also observed that the glasses can be stabilized by addition of small amounts of  $\text{GaF}_3$ ,  $\text{GdF}_3$ ,  $\text{CaF}_2$  and  $\text{NaF}$  [13].

We present here the excitation and emission spectra and lifetimes of these compositions doped with  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  as well as measurements of fluorescence line narrowing. The results obtained at room and liquid- $\text{N}_2$  temperature are compared with those obtained for the better-known fluorozirconate (ZBLAN) glass doped with  $\text{EuF}_3$ .

## 2. Experimental

### 2.1. Glass preparation

All starting reagents were fluorides with the exception of  $\text{InF}_3$  which was prepared by fluorinating  $\text{In}_2\text{O}_3$  with  $\text{NH}_4\text{F} \cdot \text{HF}$ . Glass batches were melted for 2 h at  $800^\circ\text{C}$  in a Pt crucible in a dry box. Melts were then poured between preheated ( $290^\circ\text{C}$ ) brass molds and annealed. The following compositions (in mol%) were investigated:

$34\text{InF}_3 \cdot 6\text{GaF}_3 \cdot 20\text{ZnF}_2 \cdot 20\text{SrF}_2 \cdot 15\text{BaF}_2 \cdot 2\text{NaF} \cdot 0.5\text{CaF}_2$

- (a) +  $2.5\text{GdF}_3$  (glass INF0),
- (b) +  $2.0\text{GdF}_3 \cdot 0.5\text{EuF}_3$  (glass INF1),
- (c) +  $1.5\text{GdF}_3 \cdot 1.0\text{EuF}_3$  (glass INF2),
- (d) +  $2.5\text{EuF}_3$  (glass INF3) and
- (e) +  $57\text{ZrF}_4 \cdot 28\text{BaF}_2 \cdot 3\text{LaF}_3 \cdot 5\text{AlF}_3 \cdot 0.5\text{NaF} \cdot 0.5\text{EuF}_3$  (ZBLAN).

### 2.2. Spectroscopic measurements

Excitation and emission spectra were obtained with powdered samples at room temperature and at liquid- $\text{N}_2$  temperature using a Spex Fluorolog F121I fluorimeter with excitation from a 450 W Xe lamp. Excited states decay times were obtained with the same spectrometer at room temperature with excitation from a pulsed Xe lamp (5 J/pulse, 3  $\mu\text{s}$  pulse width) and detection with a Spex 1934D phosphorimeter.

Fluorescence line narrowing data were obtained with bulk samples at liquid- $\text{N}_2$  temperature with a home-made dc rhodamine 6G dye laser pumped with a Inova 400 Coherent Ar ion laser. A Spex 1403 double monochromator coupled to a RCA 31034 cooled photomultiplier was used for signal detection.

## 3. Results and discussion

Fig. 1 shows the overall  $\text{Eu}^{3+} {}^5\text{D}_0$  level excitation spectra of the glasses investigated at liquid- $\text{N}_2$  temperature. Electronic transitions arising from  ${}^7\text{F}_0$  ground-state levels are observed for several excited states of the  $4f^6$  configuration. Tentative transition assignments based on literature values [5,8] are found in Fig. 1. No charge-transfer state could be

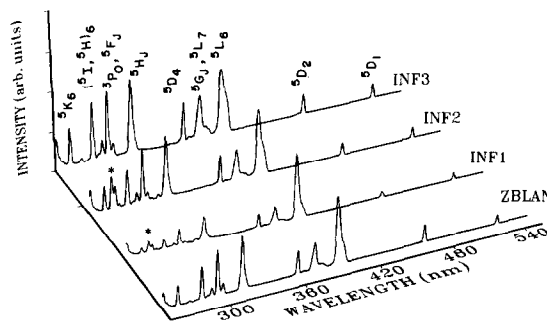


Fig. 1. LNT  $\text{Eu}^{3+} {}^5\text{D}_0$  excitation spectra ( $\lambda_{\text{em}} = 615 \text{ nm}$ ). Transitions are assigned to transitions from  ${}^7\text{F}_{0,1}$  to the  ${}^{25+1}\text{L}_J$  excited states indicated in the figure. Stars denote  $\text{Gd}^{3+}$  absorption lines.

identified up to 250 nm. In fact the Eu–F charge transfer is predicted to be located at much higher energies [14]. For the samples (INF1) and (INF2) the lines observed at 273 and 275.5 nm are assigned to the  $\text{Gd}^{3+} {}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{7/2}$  transition, revealing  $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$  energy transfer. For the three INF glasses one observes, with increasing  $\text{Eu}^{3+}$  concentration, a decrease in the relative intensity for the lines occurring at wavelengths higher than 350 nm. This phenomenon seems to be related to a concentration quenching mechanism more easily observed in the emission spectra and lifetimes, although we found no clear explanation for this behavior.

Taking the intensity ratio between the  $\Delta J = 2$  and  $\Delta J = 1$  transitions as a measure of the asymmetry for a given lanthanide environment, the transition intensity ratio  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  (464 nm) /  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$  (532 nm) is found slightly higher for ZBLAN compared to the INF glasses denoting a less-symmetric ligand field for  $\text{Eu}^{3+}$  in ZBLAN than in INF.

Fig. 2 shows a selected region of the excitation spectra for (INF1) and ZBLAN glasses (note that abscissa scale has been changed to  $\text{cm}^{-1}$ ), where vibronic lines are observed associated with the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$  ( $19040 \text{ cm}^{-1}$ ) and  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  ( $17290 \text{ cm}^{-1}$ ) electronic transitions. They are also observed with the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  transition (not shown in Fig. 2). For INF glass the vibronic lines appear at  $19360$  and  $17610 \text{ cm}^{-1}$  characterizing a  $320 \text{ cm}^{-1}$  vibrational mode. For ZBLAN two vibronic transitions are observed at  $17495$  and  $17700 \text{ cm}^{-1}$  ( $200$  and  $405 \text{ cm}^{-1}$  vibrational modes) for the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  line and one at  $19455 \text{ cm}^{-1}$  for the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$  line ( $405 \text{ cm}^{-1}$  vibrational mode). It must be pointed out that the available the-

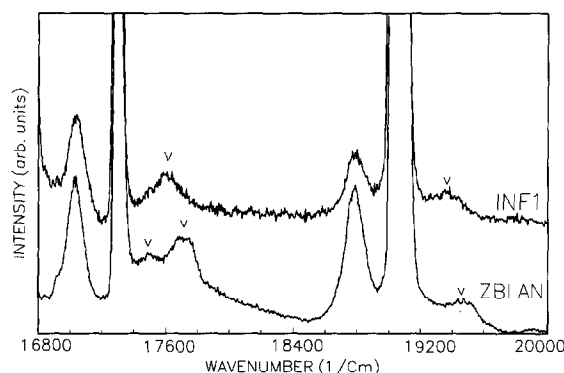


Fig. 2. LNT  $\text{Eu}^{3+}$   $^5\text{D}_0$  excitation spectra showing vibronic lines (V) associated with the  $^7\text{F}_0 \rightarrow ^5\text{D}_0$  ( $17290 \text{ cm}^{-1}$ ) and  $^7\text{F}_0 \rightarrow ^5\text{D}_1$  ( $19040 \text{ cm}^{-1}$ ) electronic transitions.

ories predict selection rules  $\Delta J = 0, \pm 2$  for vibronics. The observation of vibronics belonging to the magnetic dipole  $^7\text{F}_0 \rightarrow ^5\text{D}_1$  ( $\Delta J = +1$ ) transition may indicate classical one-phonon vibronic replicas and consequently an important Huang–Rhys parameter, which is not expected for these ionic hosts [14,15]. As usually done in the literature [10] the electron–phonon coupling parameter,  $g$ , may be evaluated by calculating the intensity ratio between the vibronic and the associated electronic lines.  $g$  values are around 0.15 for all glasses studied in this work. There is no appreciable variation in  $g$  with  $\text{Eu}^{3+}$  concentration.

Raman spectra [16] show for fluoroindate glasses a strong polarized band at  $\approx 507 \text{ cm}^{-1}$  and a broad depolarized band centered at  $\approx 203 \text{ cm}^{-1}$ . IR reflection spectra [16] show modes at  $\approx 484$  and  $225 \text{ cm}^{-1}$ . Raman spectra for ZBLAN show a polarized band at  $580 \text{ cm}^{-1}$  and several depolarized weak bands at lower frequencies [17]. As shown in Fig. 2 vibronics are related with vibrational modes with frequencies lower than the Raman or IR highest frequency modes. This feature has been assigned to a local vibration including the lanthanide ion in a simple harmonic oscillator [9]. This lowering in frequency is not observed for oxide glasses and many crystals and in fact two different types of vibronic transitions are known: those denoting a lanthanide–ligand vibrational mode and those showing molecular modes of the ligand group [14,15]. Fluoride glasses seem to fit the former case while oxide glasses show the latter case.

Fig. 3 shows the overall LNT  $\text{Eu}^{3+}$  emission spectra of the four glasses studied with  $\lambda_{\text{exc}} = 394 \text{ nm}$

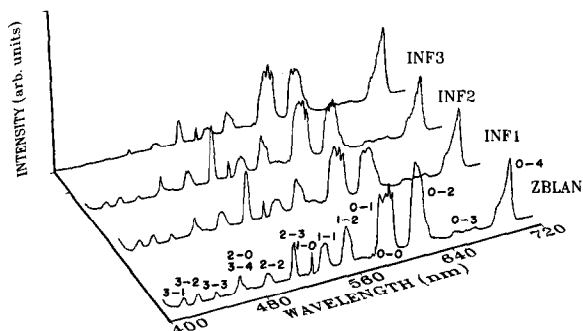


Fig. 3. LNT  $\text{Eu}^{3+}$  emission spectra.  $J$ – $J'$  labels denote transitions from the excited states  $^5\text{D}_J$  to the lower  $^7\text{F}_{J'}$  levels.

( $^7\text{F}_0 \rightarrow ^5\text{L}_6$  transition). Emission is observed from the  $^5\text{D}_J$  ( $J=0, 1, 2$  and  $3$ ) excited states to the  $^7\text{F}_{J'}$  ( $J'=0, 1, 2, 3$ , and  $4$ ) lower levels. As was done for excitation spectra, the assignments of the transitions could be done by comparing each spectrum with literature results. The emission from the higher  $^5\text{D}_J$  ( $J=2, 3$ ) is more intense in INF1 glass than in ZBLAN (same  $\text{Eu}^{3+}$  concentration). The transition  $^5\text{D}_2 \rightarrow ^7\text{F}_3$  at  $511 \text{ nm}$  is particularly very intense corroborating the calculations of Blanzat et al. [5] for the radiative transition probabilities in a fluorozirconate glass. For fluoroindates these values may not be very different and indeed, as the multiphonon decay rate is lower this transition is observed with higher intensity.

With the increase in  $\text{Eu}^{3+}$  concentration, the emission from the higher  $^5\text{D}_{2,3}$  levels is clearly quenched. Self-quenching is known to occur by ion–ion interaction in a cross-relaxation mechanism [18]. As the  $^5\text{D}_{2,3}$  levels are closely spaced there is a high probability for cross relaxation involving transitions between  $^7\text{F}_J$  lower levels, as the  $\text{Eu}^{3+}$  concentration increases [18,19].

The intensity ratio  $^5\text{D}_0 \rightarrow ^7\text{F}_2 / ^5\text{D}_0 \rightarrow ^7\text{F}_1$  is smaller for fluoroindate than for ZBLAN glasses. As already observed in the excitation spectra, the point symmetry of the  $\text{Eu}^{3+}$  environment is closer to an inversion center in fluoroindate glass than it is in ZBLAN.

Table 1 shows the decay times observed for transitions occurring from the  $\text{Eu}^{3+}$   $^5\text{D}_J$  excited-state levels at room temperature ( $\lambda_{\text{exc}} = 394 \text{ nm}$ ). Decays from the  $^5\text{D}_3$  level were always found to be non-exponential. For the other  $^5\text{D}_J$  levels there is a decrease in the lifetime values with the increase in  $\text{Eu}^{3+}$  concentration. The decay time for the  $^5\text{D}_2$  level becomes non-

Table 1  
Decay times (ms) observed for  $\text{Eu}^{3+} {}^5\text{D}_J$  and  $\text{Gd}^{3+} {}^6\text{P}_{7/2}$  levels

Level	Glass				
	INF0	INF1	INF2	INF3	ZBLAN
${}^5\text{D}_3$	–	non-exp	non-exp	non-exp	non-exp
${}^5\text{D}_2$	–	1.8	1.5	non-exp	0.9
${}^5\text{D}_1$	–	2.4	2.2	1.7	1.6
${}^5\text{D}_0$	–	7.2	7.0	6.6	5.7
${}^6\text{P}_{7/2}$	8.1	7.0	6.9	–	–

exponential for INF3 glass (higher  $\text{Eu}^{3+}$  content). The higher decay time values found for fluorindates agree with the higher point symmetry and lower phonon energies for these glasses when a comparison is made with ZBLAN.

Table 1 also shows the results for the  $\text{Gd}^{3+} {}^6\text{P}_{7/2}$  decay time observed for INF0 (without Eu), INF1, INF2 ( $\lambda_{\text{exc}} = 273 \text{ nm}$ ;  $\lambda_{\text{em}} = 312 \text{ nm}$ ). One observes a slight decrease in the decay times with the addition of  $\text{Eu}^{3+}$ . One may therefore conclude from the excitation spectra and from decay-time measurements that the energy transfer from  $\text{Gd}^{3+}$  to  $\text{Eu}^{3+}$  occurs efficiently in these hosts.

Fig. 4 shows selected emission spectra obtained with laser excitation in the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  profile for glasses

INF1 and ZBLAN. Fluorescence line narrowing is observed with great similarities between the glasses. As noted under broad-band excitation the intensity ratio  ${}^5\text{D}_0 \rightarrow {}^7\text{D}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  is also smaller for INF1.

From the observed  ${}^7\text{F}_1$  splittings some crystal field considerations may be done. Following the literature the  $B_0^2$  and  $B_2^2$  crystal field parameters have been calculated by diagonalizing the  $3 \times 3 {}^7\text{F}_1$  matrix [4] with a  $\text{C}_{2v}$  symmetry. In addition the comparison between different ligand fields is known to be better using Auzel's  $N_v$  scalar crystal field parameter [20] defined as

$$N_v = \left[ \sum_{k,q} (B_q^k)^2 \left( \frac{4\pi}{2k+1} \right) \right]^{1/2}.$$

Table 2 gathers all the results. The range of values of  $N_v$  ( $500\text{--}1500 \text{ cm}^{-1}$ ) is narrower than those observed for oxide glasses (typically  $600\text{--}2800 \text{ cm}^{-1}$ ), denoting a narrower distribution of  $\text{Eu}^{3+}$  sites in the fluoride hosts.  $N_v$  values are also higher for INF1 than ZBLAN, and this may be rationalized in terms of the compromises existing between the Zr–F and In–F and the Eu–F chemical bonds. The lower is the force constant for the Zr–F or In–F bonds, the higher it is for Eu–F, and the higher is the  $N_v$  value. From the analysis of the vibrational data the force constant was found higher for Zr–F than In–F and one concludes

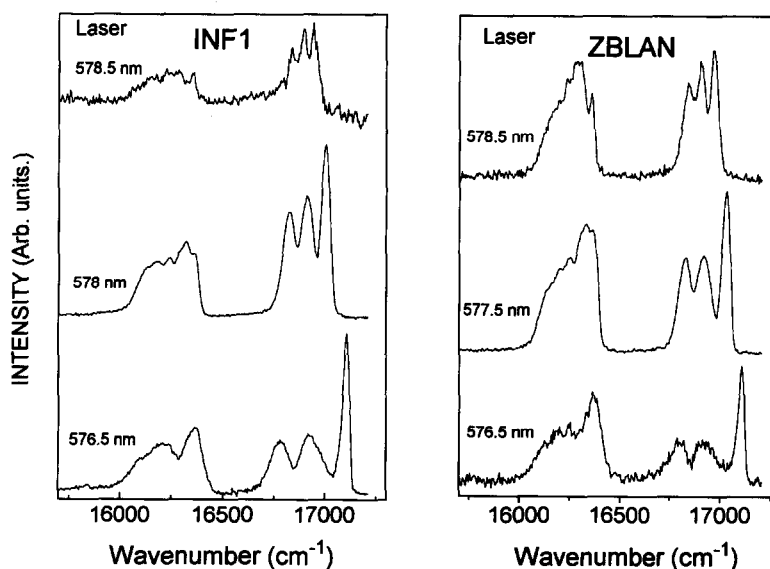


Fig. 4. Fluorescence narrowed lines obtained with laser excitation in the inhomogeneously broadened  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  transition. Excitation laser wavelengths are indicated in the figure.

Table 2

 $B_0^2$ ,  $B_2^2$  and  $N_v$  parameters ( $\text{cm}^{-1}$ ) for INF1 and ZBLAN glasses

${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ (nm)	ZBLAN			INF1		
	$B_0^2$	$B_2^2$	$N_v$	$B_0^2$	$B_2^2$	$N_v$
576.5	820	235	1401	807	310	1455
577	688	192	1171	74/24	266	1292
577.5	531	177	929	–	–	–
578	362	148	662	471	192	860
578.5	–	–	–	253	133	499

therefore that the Eu–F interaction is strengthened in fluorindate glasses.

#### 4. Conclusions

We have studied the fluorescence properties of  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  in a new indium-fluoride-based glass. Emission spectra and excited states lifetimes show quenching effects due to increase of  $\text{Eu}^{3+}$  concentration. Eu–Eu and Gd–Eu energy transfers were evidenced. Comparing the results with those obtained for the well-known ZBLAN (doped with Eu), higher decay times and higher point symmetry, closer to an inversion center are observed for the fluorindate. Lower phonon energies are observed in the vibronic structure comparing with Raman data. In contrast with oxide glass where vibronics reveal vibrational modes of the network structure, in these glasses only Eu–F or Gd–F vibrational modes are active.

From fluorescence line narrowing experiments and simple crystal-field analyses of  $B_q^k$  and  $N_v$  parameters we conclude that the Eu–F interactions are stronger in fluorindate glasses than in ZBLAN.

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